

526 Rec'd PCT/PTO 24 JAN 2001

FORM PTO-1390 (REV 12-29-99)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 1-15240	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/744420	
INTERNATIONAL APPLICATION NO. PCT/GB99/02501		INTERNATIONAL FILING DATE 29 July 1999 (29.07.99)		PRIORITY DATE CLAIMED 01 August 1998 (01.08.98)	
TITLE OF INVENTION PROCESS FOR COATING GLASS					
APPLICANT(S) FOR DO/EO/US KEVIN DAVID SANDERSON					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input checked="" type="checkbox"/> A ^{copy} translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)) and annexes, and amended sheets. 					
Items 11. to 16. below concern document(s) or information included:					
<ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment, with Exhibit A (IPEA Report) <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input checked="" type="checkbox"/> Other items or information: Express Mail Certificate; return card; formal drawings (2 sheets); a copy of the International Search Report; a copy of the cover page of the published int'l application 					

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U.S. APPLICATION NO. (If known) 09/744420 INTERNATIONAL APPLICATION NO. PCT/GB99/02501		ATTORNEY'S DOCKET NUMBER 1-15240							
17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO..... \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 <div style="text-align: right;">ENTER APPROPRIATE BASIC FEE AMOUNT =</div>		<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <th colspan="2" style="text-align: left;">CALCULATIONS</th> <th style="text-align: left;">PTO USE ONLY</th> </tr> <tr> <td colspan="2" style="height: 150px; vertical-align: top;"> <div style="text-align: right;">\$ 860.00</div> </td> <td></td> </tr> </table>		CALCULATIONS		PTO USE ONLY	<div style="text-align: right;">\$ 860.00</div>		
CALCULATIONS		PTO USE ONLY							
<div style="text-align: right;">\$ 860.00</div>									
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		<div style="text-align: right;">\$ -</div>							
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE						
Total claims	33 - 20 =	13	X \$18.00						
Independent claims	5 - 3 =	2	X \$80.00						
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00						
TOTAL OF ABOVE CALCULATIONS =			\$1,254.00						
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).			<div style="text-align: right;">\$ -</div>						
SUBTOTAL =			\$1,254.00						
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).			<div style="text-align: right;">\$ -</div>						
TOTAL NATIONAL FEE =			\$1,254.00						
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property			<div style="text-align: right;">\$ -</div>						
TOTAL FEES ENCLOSED =			\$1,254.00						
			Amount to be refunded: \$						
			charged: \$						

a. ☒ A check in the amount of **\$ 1,254.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of \$_____ to cover the above fees.
 A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. **13-1816**. ~~A duplicate copy of this sheet is enclosed.~~

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on January 24, 2001 and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Kathleen J. Moore
(Signature of person mailing correspondence)

Kathleen J. Moore
(Typed name of person mailing correspondence)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:]	
KEVIN DAVID SANDERSON]	Group Art Unit:
]	
Serial No.]	
Filed:]	Examiner:
]	
Filing Under 35 U.S.C. 371 in]	
the DO/EO/US off PCT/GB99/02501]	
filed 29 July 1999 (29.07.99)]	
]	
For: PROCESS FOR COATING GLASS]	Attorney Docket 1-15240

January 24, 2001

Assistant Commissioner for Patents
BOX PCT
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Honorable Sir:

Prior to the first Office Action, please amend the application being filed concurrently herewith under 35 U.S.C. 371 as follows:

IN THE SPECIFICATION

Page 1, above line 1, insert --TITLE--; line 2, insert --BACKGROUND OF THE INVENTION--; between lines 5 and 6, insert --Field of the Invention--; between lines 20 and 21, insert --Description of the Related Art--; between lines 12 and 13 insert --SUMMARY OF THE INVENTION--.

Page 7, between lines 17 and 18, insert --BRIEF DESCRIPTION OF THE DRAWINGS--; and between lines 27 and 28, insert --DESCRIPTION OF THE PREFERRED EMBODIMENTS--.

Page 10, line 16, insert --(0.69 MPa)-- before "pressure".

IN THE CLAIMS

Please amend the claims as follows:

1. (Amended) A process for depositing a coating comprising tungsten oxide on the surface of a glass substrate by directing a gaseous stream comprising tungsten oxyhalide or tungsten chloride and a source of oxygen on to the surface of the glass substrate, wherein the glass substrate is at a temperature in the range 500°C to 720°C.

Claim 3, line 1, delete "or claim 2".

Claims 4, 5, 8, 9, 10, 12, 15, 17, 18, 19 and 23, line 1, delete "any preceding" and insert --1-- after "claim".

Claim 7, line 1, delete "or 6".

Claim 14, line 1, delete "or 13".

20. (Amended) A process for coating glass comprising directing a gaseous stream containing a tungsten compound and a source of oxygen on to the surface of a glass substrate thereby forming a non-stoichiometric tungsten oxide layer [characterised in that] wherein the tungsten oxide layer is [non-stoichiometric and the tungsten oxide layer is] overcoated with a further layer.

Claim 21, line 1, delete "19 or".

Claim 22, line 1, delete "claims 19 to 21" and insert --claim 20-- after "to".

Delete original claims 24 to 33 and insert the following new claims:

34. A process according to claim 1 wherein the glass substrate is at a temperature in the range 565°C to 655°C.
35. A process according to claim 1 wherein the tungsten oxide layer is deposited on to coated glass.

36. A process according to claim 35 wherein the coated glass has a coating comprising silicon oxide.
37. A process according to claim 36 wherein the coating comprising silicon oxide further contains carbon.
38. A process for coating glass comprising entraining a tungsten compound in a gas by flowing the gas over a tungsten compound at a temperature below its melting point and directing the gaseous stream on to the surface of a glass substrate thereby forming a tungsten oxide layer, wherein the glass substrate is at a temperature in the range of 500°C to 720°C.
39. A process according to claim 38 wherein the tungsten compound is tungsten halide, tungsten oxyhalide or tungsten carbonyl.

40. A method of coating glass comprising
- (a) providing a glass substrate having a temperature in the range of 500°C to 720°C,
 - (b) preparing a gaseous stream comprising a source of oxygen and a tungsten compound selected from the group consisting essentially of tungsten oxyhalide and tungsten chloride, and
 - (c) directing the gaseous stream on to the glass substrate, thereby depositing a coating comprising tungsten oxide on the glass substrate.
41. A process for depositing a coating comprising tungsten oxide on the surface of a glass substrate by directing a gaseous stream comprising tungsten oxyhalide or tungsten chloride and an ester on to the surface of the glass substrate.
42. A coated glass produced by a process according to claim 1.
43. A multiple glazing unit comprising a coated glass according to claim 42 in spaced opposed relation to a glazing pane.

IN THE ABSTRACT

Page 20, line 3, delete "Process for Coating Glass"; line 15, delete "FIGURE 1".

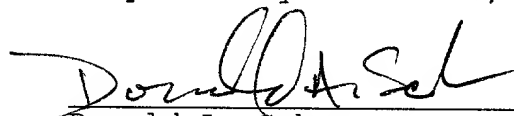
REMARKS

Applicants have amended the application to eliminate multiple dependencies, to incorporate the amendments filed in the European Patent Office on September 28, 2000, in PCT/GB99/02501, the priority of which is claimed (copy attached hereto as Exhibit A), and to adapt the specification, claims and abstract to U.S. patent practice.

Original claims 24-33 have been deleted. New claims 34-43 have been added. Claims 1-23 and 34-43 are currently pending in the present application. No new matter has been added by any of the above amendments.

Favorable consideration of the application as amended is respectfully requested.

Respectfully submitted,


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PROCESS FOR COATING GLASS

This invention relates to a process for coating glass and a coated glass, in particular it relates to a process for depositing a tungsten oxide layer on to glass.

There is a demand for solar control glass, that is glass which transmits a high percentage of incident light and a relatively low percentage of total incident radiation energy (total solar heat). One way of producing such a glass is by depositing on to glass a coating comprising a layer or layers of various materials, in particular metal oxides, the layers usually having thicknesses in the submicrometer range. A convenient deposition method for metal oxide coatings on glass is on-line chemical vapour deposition which comprises directing a gaseous stream of a metal containing compound and an oxygen containing gas (often water) on to a hot glass ribbon as the ribbon is produced, the components of the gaseous stream react together at the hot glass surface and deposit a metal oxide layer.

A metal oxide useful in glass coatings, including solar control coatings, is tungsten oxide, known in stoichiometric, non-stoichiometric and doped forms. EP 0 546 669 B1 describes a method for the deposition of fluorine doped tungsten oxide on to the surface of a glass sheet by chemical vapour deposition during the float glass production process. The method comprises reacting tungsten hexafluoride with an oxygen containing compound and a fluorine containing tungsten compound adjacent the surface of a hot glass ribbon at a temperature of 350°C to 450°C and for a time sufficient to produce a layer of $WO_{3-x}F_x$ (x is said to be from greater than zero to less than one). Unfortunately, EP 0 546 669 B1 does not provide a simple

general process for depositing tungsten oxide (i.e. an adaptable process that can be used to deposit tungsten oxide, including stoichiometric and non-stoichiometric tungsten oxide as well as doped tungsten oxide).

5 High coating growth rate is desirable for a coating process. To achieve this in chemical vapour deposition of tungsten oxide layers, it is desirable that the tungsten compounds (and other components of the gas stream) have a relatively high volatility (which helps in achieving good
10 carryover of the tungsten compound to the glass surface), and good thermal stability (to alleviate thermal decomposition before reaching the glass surface).

We have discovered, in accordance with the present invention, a simple chemical vapour deposition process for
15 the deposition of tungsten oxide layers in stoichiometric, non-stoichiometric or doped forms that can be conveniently used to deposit tungsten oxide on-line during the glass production process at high coating growth rates.

20 According to an aspect of the present invention there is provided a process for depositing a coating comprising tungsten oxide on the surface of a glass substrate by directing a gaseous stream comprising tungsten oxyhalide or tungsten chloride and a source of oxygen on to the surface of the glass substrate.

25 Preferably, the coating comprising tungsten oxide comprises a layer of tungsten oxide.

Preferably the tungsten oxyhalide is tungsten oxychloride, more preferably tungsten oxytetrachloride (WOCl_4). Alternatively, tungsten oxyhalide may comprise
30 tungsten dioxydichloride (WO_2Cl_2) which is the product of reaction between WOCl_4 and water (and is often present as an impurity in WOCl_4). The volatility and thermal stability of tungsten oxytetrachloride are such as to

provide good carryover to the glass surface without significant thermal degradation.

Usually tungsten chloride will be tungsten (V) chloride (WCl_5) or tungsten (VI) chloride (WCl_6).

5 The tungsten oxyhalide or tungsten chloride may be a substituted tungsten oxyhalide or tungsten chloride. Generally any substituted tungsten oxyhalide or tungsten chloride or mixture of tungsten oxyhalides or tungsten chlorides and/or substituted tungsten oxyhalides or
10 tungsten chlorides may be used in the invention including for example $WX_{6-n}(OR)_n$, $WOX_{4-n}(OR)_n$, (where $X = Cl, Br, I$ or F and R is an organic group and n is an integer preferably having a value in the range 1-3), or tungsten oxyhalide substituted with multidentate ligands.

15 Preferably the source of oxygen is an ester, especially an ester with 4 to 10 carbon atoms, more preferably an ester with 3 or 4 to 6 carbon atoms, most preferably ethyl acetate or butyl acetate. The use of esters as sources of oxygen appears to have the effect of
20 increasing the deposition rate of tungsten oxide with incorporation of oxygen from the ester into the coating. It is thought that this is because the ester decomposes at elevated temperature first to a carboxylic acid and then to water. The decomposition temperature of 3 to 6 carbon atom
25 esters appears to be such that most of the decomposition occurs in or near the surface of the substrate, rather than in the delivery lines, with the result that the reaction of water and tungsten precursors occurs more at the glass surface, enhancing deposition rate and reducing pre-
30 reaction and blocking of the delivery lines. Blocking of the delivery lines may especially occur if free water is present in the delivery lines including water present as a result of too early a decomposition of an ester.

The gaseous stream may contain oxygen gas, which has the advantage of producing tungsten oxide coatings with significantly lower haze.

5 The ratio of tungsten oxyhalide or tungsten chloride and the source of oxygen are desirably such that the layer of tungsten oxide is deposited as non-stoichiometric tungsten oxide (i.e. a ratio having less than the stoichiometric amount of oxygen, producing an oxygen deficient tungsten oxide). Non-stoichiometric tungsten
10 oxide (represented as WO_{3-x} where x is greater than zero but usually less than 0.5), tends to absorb infra red radiation with little absorption of visible light when x is of a suitable value which may be, for example, up to about 0.03. Non-stoichiometric tungsten oxide is particularly useful as
15 a layer coating intended for solar control applications.

The gaseous stream may contain a source or sources of fluorine which is advantageous if it is desired to produce fluorine doped tungsten oxide. Preferably the source of fluorine is hexafluoropropylene oxide or trifluoroacetic
20 acid, more preferably hexafluoroethane. Hexafluoroethane is especially preferred because its use provides substantially haze free fluorine doped tungsten oxide coatings.

In a preferred aspect of the invention tungsten
25 oxyhalide or tungsten chloride is entrained in a gaseous stream by flowing gas over hot tungsten oxyhalide or tungsten chloride, preferably whilst tungsten oxyhalide or tungsten chloride is at a temperature in the range 170°C to 210°C. In this range of temperatures tungsten
30 oxytetrachloride does not have a defined liquid region, but surprisingly, despite being substantially solid, tungsten oxytetrachloride is entrained in the flowing inert gas sufficiently well to provide good carryover to the surface

of the glass substrate. At temperatures lower than 170°C carryover is low which can result in low growth rate, above 210°C decomposition of the precursor may result, especially during prolonged heating. The flowing gas preferably comprises nitrogen.

The process of the present invention is normally used to deposit tungsten oxide coatings having thicknesses in the range 70 to 180 nm and commonly enables growth rates of tungsten oxide in the range 3 to 25 nm s⁻¹ to be achieved.

The tungsten oxide layer may be overcoated with a further layer, the further layer may be a metal oxide layer, preferably fluorine doped tin oxide. This aspect provides protection of the tungsten oxide layer from degradation (for example, from oxidation or weathering) and if the further layer is fluorine doped tin oxide has the additional advantage of providing a solar control coating, with low emissivity (high infra red reflection), and is applicable whether the tungsten oxide layer is formed from a tungsten oxyhalide or a tungsten chloride or otherwise.

Thus, according to a further aspect of the invention, there is provided a process for coating glass which comprises directing a gaseous stream containing a tungsten compound and a source of oxygen on to the surface of a glass substrate thereby forming a tungsten oxide layer characterised in that the tungsten oxide layer is non-stoichiometric and the tungsten oxide layer is overcoated with a further layer. Generally, in this aspect of the invention, any suitable tungsten compound and source of oxygen may be used to form a tungsten oxide layer which is non-stoichiometric and which is overcoated by a further layer. The tungsten compound and source of oxygen need not be separate compounds (i.e. a tungsten oxygenate may be used).

Each aspect of the present invention may be performed during the float glass production process, which is advantageous because coated glass according to the invention may then be continuously produced.

5 Each aspect will normally be performed where the glass substrate is at a temperature in the range 500°C to 720°C, which is practical with the preferred tungsten precursors of the invention (tungsten oxyhalide or tungsten chloride) and this temperature range facilitates achieving a high
10 deposition rate and a durable coating. The most usual temperature range is 565°C to 655°C.

The glass substrate will normally be soda lime silica glass because this is commonly produced during the float glass production process. Unfortunately, when soda-lime-silica glass is used as a substrate, there is a tendency
15 for alkali metal ions from the glass to migrate into the coating; this has two potential deleterious effects. First, the introduction of sodium ions into the coating is liable to modify the electronic characteristics of the
20 tungsten oxide affecting its optical properties. Second, when a halogen-containing, especially a chlorine-containing, precursor has been used to deposit the tungsten oxide, sodium ions may react with halogen residues incorporated in the coating forming sodium halide crystals
25 resulting in the coating having a hazy appearance. Such sodium migration may be combated by depositing an alkali-blocking interlayer on the glass for example of silica, or a silicon oxycarbide. Moreover, by appropriate selection and control of the underlayer thickness and refractive
30 index (see for example, UK patents 2 031 756B and 2 199 848B) a colour suppression effect may be achieved i.e. the appearance of iridescence effects resulting from a thin film of tungsten oxide may be alleviated or avoided.

In another aspect, the present invention provides a method of coating glass comprising

(a) providing a glass substrate,

(b) preparing a gaseous stream comprising a source of oxygen and a tungsten compound selected from the group consisting essentially of tungsten oxyhalide and tungsten chloride, and

(c) directing the gaseous stream on to the glass substrate, thereby depositing a coating comprising tungsten oxide on the glass substrate.

The process of the present invention may be used to deposit a mixed metal oxide comprising tungsten oxide and one or more other metal oxides, for example by adding the precursor of another metal oxide to the gaseous stream.

Coated glass produced according to the invention may be used in many areas of glass use, including as a glazing pane in multiple glazing units.

In order that the invention may be better understood, reference will now be made to the drawings in which:

Figure 1 illustrates schematically an example of a static chemical vapour deposition reactor and gas delivery system useful for preparing coated glass according to the invention and as used in Examples 1-3.

Figure 2 illustrates schematically a vertical section through a vapourizer used to entrain precursors in carrier gas where the precursors are solid or substantially solid, and as used in Examples 4-6.

Referring to Figure 1, a static chemical vapour deposition reactor and gas delivery system, generally designated 1, comprises a reactor having an outlet line 23 and an inlet line 22 both of which may be wound and heated with heating tape to reduce the likelihood of condensation. The line 22 continues 20 into the oven 8 and connects to a

four-way valve. The oven 8 has an even temperature profile throughout to reduce hot spots/thermal decomposition and reduce cold spots/condensation. The other connections to the four-way valve are the line 17 to a purge gas source, a line 21 to a waste furnace, and a line 19 to a tungsten precursor bubbler (bubbler 1). Leading off from the line 19 a line 15 is partly in the oven but exits and is connected to additive bubbler 2 and bubbler 3 by lines 13 and 11 respectively. A motorized and heated syringe driver enables the introduction and vapourization of precursor/additive solutions.

Referring to Figure 2, a vapourizer 25 for use with volatile solid precursor comprises an inlet 24 for carrier gas connecting to the vapourizer vessel 27 via a channel 26 leading to a chamber inlet 28 at the base of the vapourizer vessel 27. The chamber 28 inlet allows the carrier gas to enter the interior 29 of the vapourizer chamber 27. Inside the vapourizer chamber are positioned plural meshed shelves 30, with a mesh size small enough to prevent solid precursor particles or powder 31 from falling through, and hence keeping the interior of the chamber 29 near the chamber inlet 28 free of precursors that could sinter and reduce or prevent gas flow into the vapourizer. Above the shelves is a carrier gas outlet 32 for connection to gas delivery lines and thence reactors (not shown). In use, the vapourizer would be heated.

The invention is illustrated by the following Examples.

Examples 1-3

In this series of Examples a tungsten oxide coating was deposited on to the face of a float glass substrate carrying a colour suppressing/alkali blocking silicon oxide layer containing carbon (produced as described in European

patent EP 0 275 662B) using a laboratory static chemical vapour deposition reactor and gas delivery system as illustrated in Figure 1 and described above. In the reactor, the glass substrate was supported on a cartridge heated graphite block and heated to provide a glass temperature of 625°C. The tungsten precursor was tungsten oxytetrachloride (WOCl_4) which is an orange solid with a melting point of approximately 211°C, and is air sensitive undergoing a reaction with moisture to form tungsten dioxydichloride (WO_2Cl_2) a yellow solid with lower volatility usually present as an impurity in WOCl_4 .

A nitrogen carrier gas feed was passed through a bubbler (corresponding to bubbler 2 in Figure 1) maintained at a temperature of 30°C at a flow rate of 1 litre/min, the bubbler containing either ethyl or butyl acetate. A separate nitrogen carrier gas feed was passed over solid WOCl_4 in a standard bubbler (bubbler 1), the bubbler situated in an oven 8 to maintain the precursor in a temperature range 170 - 185°C. Thermal decomposition of WOCl_4 is low and good precursor transport and growth was still achieved after 20 hours in this temperature range. The separate carrier gas feeds, one with entrained ester and the other with entrained WOCl_4 , were combined to form a precursor gas mixture. A nitrogen make-up of 5.5 litres/min and oxygen gas were added to dilute the precursor gas mixture and the diluted precursor gas mixture was delivered through a line (20) to the reactor, the line maintained at a temperature of 200°C. The diluted precursor gas mixture was directed on to the heated glass substrate in the reactor resulting in the deposition of a tungsten oxide coating. The deposition process was continued for a run time of 10 or 30 seconds. At the end of the deposition process, the coated glass was allowed to cool to room

temperature under nitrogen. The thickness of the tungsten oxide coating was measured by standard optical (optical constants were obtained from the spectra and the spectra modelled to determine the larger thicknesses) and/or stylus methods. Similar methods were used to measure all layer thicknesses in the Examples.

Table 1 shows the ester used in each Example together with the flow rate of oxygen added to the precursor gas mixture, the run time of the coating process, the thickness of tungsten oxide deposited and the peak growth rate (growth rate of the thickest part of the layer) of the tungsten oxide coating. It was observed that for constant ethyl acetate concentration, growth rate dropped with increasing oxygen concentration.

Bubbler 1 was fitted with a 100 pound per square inch pressure relief valve to minimise risk from over-pressurisation, which could occur, for example, if there were any blockage of the bubbler or delivery lines. Particular care was taken to exclude moisture from the delivery lines and WOCl_4 bubbler because the precursor appears to have an increased sensitivity to moisture at elevated temperature.

The coating process appeared to be affected significantly by substrate temperature. During preparation and performance of these Examples the best deposition temperature range appeared to be 565 - 655°C.

TABLE I

Example	Source of Oxygen	Run Time (sec)	Oxygen Flow (L/min)	Tungsten Oxide Layer Thickness (nm)	Peak Growth Rate (nm sec ⁻¹)
1	Ethyl acetate	10	1	102	10
2	Ethyl acetate	10	0.2	180	18
3	n Butyl acetate	30	0.25	<80	2.7

Examples 4-6

In this series of Examples coatings were applied by laminar flow chemical vapour deposition in the bath on to a moving ribbon of float glass during the glass production process using laminar flow coating apparatus generally as described and illustrated in UK patent GB 1 507 996B but with features allowing the mixing of two gas streams at the coater head and dual flow coating. The glass ribbon was coated across a width of approximately 10 cm.

Before deposition of the tungsten oxide coating a silicon oxide undercoat was deposited on the glass using a water cooled graphite head coater, using a process in accordance with European patent EP 0 275 662B. The components and gas flow for the undercoat deposition were as follows: silane (0.06 litres/min), ethylene (0.36 litres/min), oxygen gas (0.16 litres/min) and nitrogen carrier gas (8 litres/min).

The tungsten oxide coating was applied by mixing two gas streams at the coater head, one stream containing tungsten oxytetrachloride (WOCl₄) as tungsten precursor and nitrogen carrier gas and the second stream containing ethyl

acetate, oxygen gas and nitrogen carrier gas, and in Example 6, a source of fluorine.

In Example 4 the line speed of the float glass ribbon was 254 metres/hour and the temperature of the glass ribbon on exit from the float bath was 604°C. Nitrogen carrier gas (1 litre/min) was passed through a vapourizer containing WOCl_4 held at a temperature of 175°C. The vaporizer design (enabling high carryover of precursor) was as illustrated in Figure 2 and described above. Entrained tungsten oxychloride was delivered to a dual flow oil-cooled coater head held at a temperature of 210°C. The gas mixture contacted and flowed parallel to the glass surface both upstream and downstream along the glass ribbon. The path of travel both upstream and downstream was about 15 cm. At the coater head the WOCl_4 gas mixture was mixed with a gas mixture containing ethyl acetate (as oxygen source) entrained by passing nitrogen (flow rate 1.2 litres/min) through a bubbler containing ethyl acetate held at a temperature of 42°C, and oxygen gas (flow rate 0.2 litres/min). The WOCl_4 gas stream was diluted by a flow make-up of 4 litres/min and the ethyl acetate gas stream by a flow make-up of 3 litres/min. The growth rate of the tungsten oxide coating was approximately 25 nm/second, yielding a tungsten oxide layer thickness of approximately 110 nm. The thickness of the silicon oxide underlayer was approximately 45 nm. It was noticed that as the strip of tungsten oxide coated glass in Example 4 passed down the float glass production line, the blue colour of the coated glass (thought to indicate a non-stoichiometric tungsten oxide coating) gradually lessened. It is thought that this is due to oxidation or other change in stoichiometry of the tungsten oxide coating in an oxidising atmosphere at elevated temperature because this effect was not seen in

Examples 1-3 which were cooled under nitrogen. To alleviate the degradation of the tungsten oxide coating, an overcoat of fluorine doped tin oxide was applied in Examples 5 and 6.

5 The conditions for deposition of the tungsten oxide coatings of Examples 5 and 6 were similar to Example 4 and described in Table 2. In Example 6 a fluorine dopant (hexafluoroethane) was added to the second gas mixture in order to produce fluorine doped tungsten oxide. Other
10 fluorine dopants (trifluoroacetic acid and hexafluoropropylene oxide) had been briefly added to the coating gases, but increased the haze of the coated glass under the conditions used for deposition.

15 The fluorine doped tin oxide layer overcoating the tungsten oxide layer in Examples 5 and 6 was deposited just after deposition of the tungsten oxide layer in the float bath. The tin precursor used was dimethyl tin (IV) dichloride ($(\text{CH}_3)_2\text{SnCl}_2$) entrained in the carrier gas (flow rate 0.6 litres/min) by passing nitrogen through a bubbler
20 held at 150°C and delivered to the coater head through a delivery line held at 180°C. Other lines delivered water vapour entrained in nitrogen carrier gas (flow rate 0.6 litres/min, bubbler temperature 50°C) to the coater head where the gas streams were mixed. The total nitrogen
25 carrier gas flow make-up was 5 litres/min, and 0.6 litres/min of oxygen gas was added to the gas mixture. The thickness of the deposited fluorine doped tin oxide layer is shown in Table 3. The sheet resistance of the fluorine doped tin oxide layer was about 80-120 Ω per square
30 (measured by standard methods).

The coated glasses were optically analysed and values of total solar heat transmission (TSHT) and visible

transmission were derived using standard procedures. The coated glasses had haze in the range 1% to 2%, total solar heat transmission 53% (Example 5) and 56% (Example 6) visible transmission 63% (Examples 5 and 6).

TABLE 2

	EXAMPLE 5	EXAMPLE 6
Bath exit temperature (°C)	628	628
Line speed (metres/hour)	160	160
WOCl ₄ line temperature (°C)	210	210
Ethyl acetate line temperature (°C)	160	160
Coater Head Temperature (°C)	210	210
WOCl ₄ vapourizer temperature (°C)	175	175
Ethyl acetate bubbler temperature (°C)	42	42
Nitrogen flow (WOCl ₄ bubbler) (litres/min)	1	1
Nitrogen flow (ethyl acetate bubbler) (litres/min)	1.2	1.2
Nitrogen flow (WOCl ₄ make-up) (litres/min)	4	4
Nitrogen flow (ethyl acetate make-up) (litres/min)	3	3
Oxygen gas flow (litres/min)	0.2	0.05
Hexafluoroethane gas flow (litres/min)	-	0.2
Thickness of silicon oxide layer (nm)	30	30
Thickness of tungsten oxide layer (nm)	150	170
Growth rate of tungsten oxide layer (nm/second)	21	24
Thickness of fluorine doped tin oxide layer (nm)	180	180

CLAIMS

1. A process for depositing a coating comprising tungsten oxide on the surface of a glass substrate by directing a gaseous stream comprising tungsten oxyhalide or tungsten chloride and a source of oxygen on to the surface of the glass substrate.
2. A process according to claim 1 wherein the coating comprising tungsten oxide comprises a layer of tungsten oxide.
3. A process according to claim 1 or claim 2 wherein tungsten oxyhalide comprises a tungsten oxychloride, preferably tungsten oxytetrachloride.
4. A process according to any preceding claim wherein tungsten oxyhalide or tungsten chloride comprises a substituted tungsten oxyhalide or tungsten chloride.
5. A process according to any preceding claim wherein the source of oxygen comprises an ester.
6. A process according to claim 5 wherein the ester has from 3 to 6 carbon atoms.
7. A process according to claim 5 or 6 wherein the ester is ethyl acetate or butyl acetate.
8. A process according to any preceding claim wherein the gaseous stream contains oxygen gas.

9. A process according to any preceding claim wherein the ratio of tungsten oxyhalide or tungsten chloride and the source of oxygen are such that the layer of tungsten oxide is deposited as non-stoichiometric tungsten oxide.

10. A process according to any preceding claim wherein the gaseous stream contains a source of fluorine.

11. A process according to claim 10 wherein the source of fluorine comprises hexafluoroethane, trifluoroacetic acid or hexafluoropropylene oxide.

12. A process according to any preceding claim wherein tungsten oxyhalide or tungsten chloride is entrained in the gaseous stream by flowing inert gas over hot tungsten oxyhalide or tungsten chloride.

13. A process according to claim 12 wherein tungsten oxyhalide or tungsten chloride is at a temperature in the range 170°C to 210°C.

14. A process according to claim 12 or 13 wherein the inert gas comprises nitrogen.

15. A process according to any preceding claim wherein the source of oxygen comprises an ester and is entrained in the gaseous stream by contacting said ester with a flowing inert gas.

16. A process according to claim 15 wherein the ester is at a temperature in the range 30°C to 45°C.. ..

17. A process according to any preceding claim wherein the tungsten oxide layer has a thickness in the range 70 to 180 nm.

5 18. A process according to any preceding claim wherein the tungsten oxide layer is deposited at a growth rate in the range 3 to 25 nm s⁻¹.

10 19. A process according to any preceding claim wherein the tungsten oxide layer is overcoated with a further layer.

15 20. A process for coating glass comprising directing a gaseous stream containing a tungsten compound and a source of oxygen on to the surface of a glass substrate thereby forming a tungsten oxide layer characterised in that the tungsten oxide layer is non-stoichiometric and the tungsten oxide layer is overcoated with a further layer.

20 21. A process according to claim 19 or 20 wherein the further layer comprises a metal oxide.

25 22. A process according to claims 19 to 21 wherein the further layer comprises fluorine doped tin oxide.

30 23. A process according to any preceding claim wherein the process is performed during the float glass production process.

24. A process according to any preceding claim wherein the glass substrate is at a temperature in the range 500°C to 720°C.

5 25. A process according to any preceding claim wherein the glass substrate is at a temperature in the range 565°C to 655°C.

10 26. A process according to any preceding claim wherein the tungsten oxide layer is deposited on to coated glass.

15 27. A process according to claim 26 wherein the coated glass has a coating comprising silicon oxide, preferably containing carbon.

20 28. A process for coating glass comprising entraining a tungsten compound in a gas by flowing the gas over a tungsten compound at a temperature below its melting point and directing the gaseous stream on to a glass surface thereby forming a tungsten oxide layer.

25 29. A process according to claim 28 wherein the tungsten compound is tungsten halide, tungsten oxyhalide or tungsten carbonyl.

30

30. A method of coating glass comprising
- (a) providing a glass substrate,
 - (b) preparing a gaseous stream comprising a source of oxygen and a tungsten compound selected from the group consisting essentially of tungsten oxyhalide and tungsten chloride, and
 - (c) directing the gaseous stream on to the glass substrate, thereby depositing a coating comprising tungsten oxide on the glass substrate.
31. A coated glass produced by a process according to any preceding claim.
32. A multiple glazing unit comprising a coated glass according to claim 31 in spaced opposed relation to a glazing pane.
33. A process substantially as herein described with particular reference to any of the Examples 1 - 6.

5 A process for coating glass with a layer of tungsten
oxide comprising directing a gaseous stream containing
tungsten oxyhalide or tungsten chloride and a source of
oxygen on to the surface of a glass substrate. Preferably,
the source of oxygen comprises an ester, in particular an
10 ester having from 3 to 6 carbon atoms. The gaseous stream
may additionally contain a source of fluorine to form
fluorine doped tungsten oxide layers.

FIGURE 1

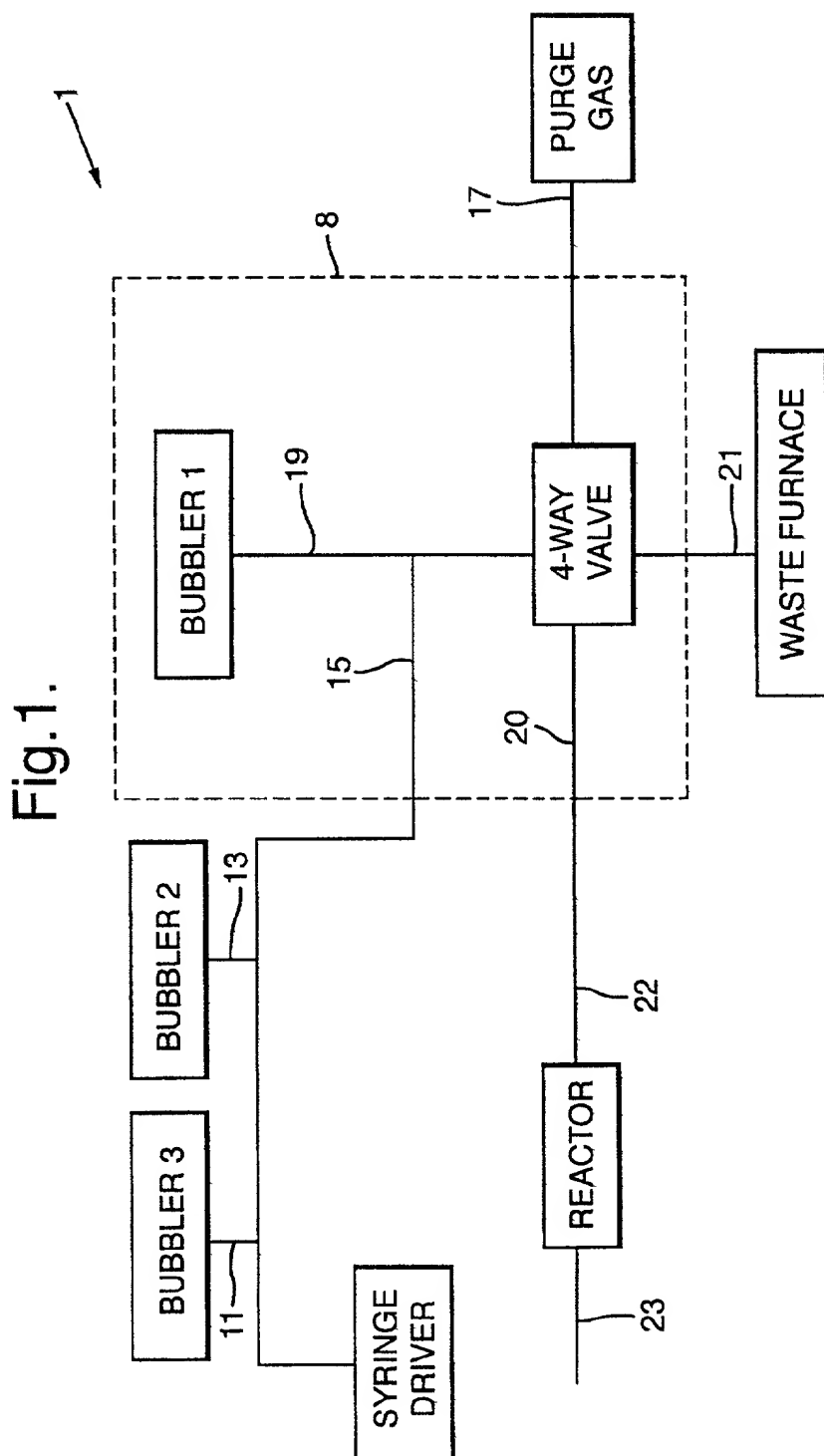
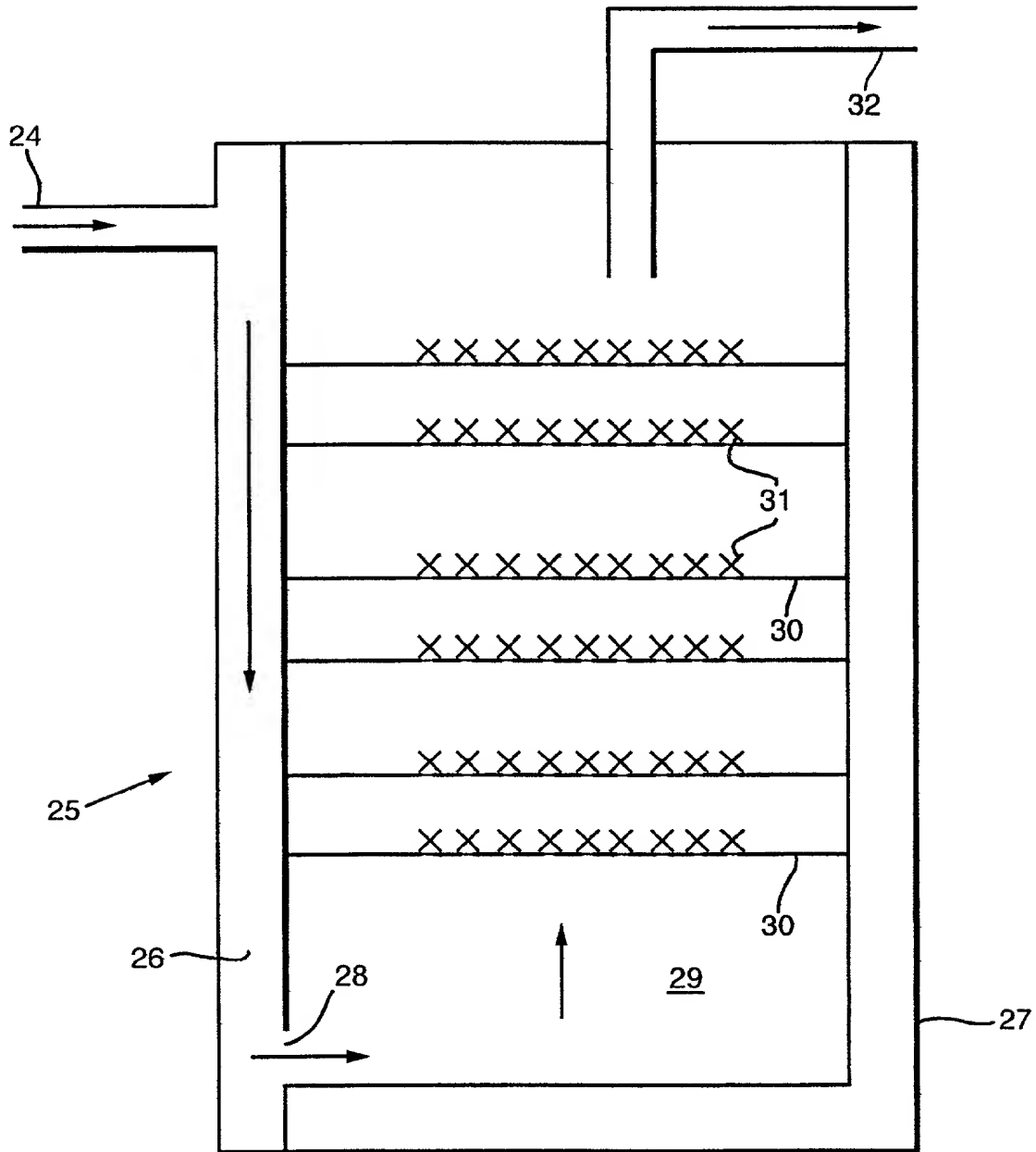


Fig.2.



COMBINED DECLARATION AND POWER OF ATTORNEY
IN ORIGINAL APPLICATION

ATTORNEY DOCKET
NO. 1-15240

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name,

I believe that I am the original, first, and sole inventor (if only one name is listed below) or an original, first, and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROCESS FOR COATING GLASS

the specification of which

(check one) is attached hereto.

 X was filed on _____
as U.S. Serial No. 09/744,420
and was amended on January 24, 2001.

 X was filed on 29 July 1999
as PCT Int'l Application No. PCT/GB99/02501
and was amended on September 28, 2000.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, § 1.56,

 X and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent; and

 if this is a continuation-in-part application, information that occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application, in accordance with 37 CFR 1.63(e); and

 in compliance with this duty, there is attached an information disclosure statement, in accordance with 37 CFR 1.98.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
9816720.8	United Kingdom	1 August 1998	X	
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

PCT/GB99/02501	29 July 1999	Pending
(Appln. Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)
(Appln. Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith with full power of substitution and revocation: Phillip S. Oberlin, Reg. No. 19,066; D. Edward Dolgorukov, Reg. No. 26,266; Donald A. Schurr, Reg. No. 34,247; Stephen P. Evans, Reg. No. 47,281; Angelica M. Colwell, Reg. No. 46,637; Patrick D. Floyd, Reg. No. 39,671; and Mark A. Hixon, Reg. No. 44,766. Address all telephone calls to Donald A. Schurr at telephone number (419) 249-7145. Address all correspondence to MARSHALL & MELHORN, Four Seagate - 8th Floor, Toledo, Ohio 43604, Attention: Donald A. Schurr.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor KEVIN DAVID SANDERSON

Inventor's signature K.D.S. - 1 - - Date 16th Jan 2001
January 16, 2001

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Full name of second joint inventor, if any _____

Second Inventor's signature _____ Date _____

Residence _____

Citizenship _____ Post Office Address _____

Full name of third joint inventor, if any _____

Third Inventor's signature _____ Date _____

Residence _____

Citizenship _____ Post Office Address _____

Full name of fourth joint inventor, if any _____

Fourth Inventor's signature _____ Date _____

Residence _____

Citizenship _____ Post Office Address _____

Attorney's Docket No. 1-15240

PATENT

For: ☒ U.S. and/or ☐ Foreign Rights
For: ☒ U.S. Application or
☐ U.S. Provisional Application
For: ☐ U.S. Patent
For: ☐ PCT Application
By: ☒ Inventor(s) or ☐ Present Owner

ASSIGNMENT OF INVENTION

In consideration of the payment by ASSIGNEE to ASSIGNOR of the sum of One Dollar (\$1.00), the receipt of which is hereby acknowledged, and for other good and valuable consideration,

ASSIGNOR:

Inventor(s) or person(s) or
entity(ies) who own the
invention

KEVIN DAVID SANDERSON
(type or print name(s) of ASSIGNOR(S))

5 Dewberry Fields

Address

Upholland, Lancs, WN8 OBQ

United Kingdom

Nationality British Subject

*(if assignment is by person or entity to whom invention was previously assigned
and this was recorded in PTO, add the following)*

Recorded on _____

Reel _____

Frame _____

hereby sells, assigns and transfers to

ASSIGNEE:

PILKINGTON PLC
(type or print name(s) of ASSIGNEE(S))

Address Prescot Road, St Helens,
Merseyside WA10 3TT

United Kingdom

Incorporated in England
Nationality

and the successors, assigns and legal representatives of the ASSIGNEE

(complete one of the following)

- ☒ the entire right, title and interest
☐ an undivided _____ percent (_____%) interest

for the United States and its territorial possessions

(check the following box, if foreign rights are also to be assigned)

- ☐ and in all foreign countries, including all rights to claim priority,
in and to any and all improvements which are disclosed in the invention entitled:

PROCESS FOR COATING GLASS

Name of inventor(s) KEVIN DAVID SANDERSON

(check and complete (a), (b), (c), (d), (e), (f) or (g))

and which is found in

- (a) ☐ U.S. patent application executed on even date herewith
(b) ☐ U.S. patent application executed on _____
(c) ☐ U.S. provisional application naming the above inventor(s) for the above-entitled invention.
☐ Express mail label no.: _____
Mailed: _____
☐ To comply with 37 CFR 3.21 for recordal of this assignment, I, an ASSIGNOR signing below, hereby authorize and request my attorney to insert below the filing date and application number when they become known.
(d) ☒ U.S. application no. 09 / 744,420
filed on _____
(e) ☒ International application no. PCT/ GB99 / 02501
(f) ☐ U.S. patent no. _____ issued _____
☐ A change of address to which correspondence is to be sent regarding patent maintenance fees is being sent separately.

(also check (g), if foreign application(s) is also being assigned)

- (g) ☐ and any legal equivalent thereof in a foreign country, including the right to claim priority

and, in and to, all Letters Patent to be obtained for said invention by the above application or any continuation, division, renewal, or substitute thereof, and as to letters patent any reissue or re-examination thereof

ASSIGNOR hereby covenants that no assignment, sale, agreement or encumbrance has been or will be made or entered into which would conflict with this assignment;

ASSIGNOR further covenants that ASSIGNEE will, upon its request, be provided promptly with all pertinent facts and documents relating to said invention and said Letters Patent and legal equivalents as may be known and accessible to ASSIGNOR and will testify as to the same in any interference, litigation or proceeding related thereto and will promptly execute and deliver to ASSIGNEE or its legal representatives any and all papers, instruments or affidavits required to apply for, obtain, maintain, issue and enforce said application, said invention and said Letters Patent and said equivalents thereof which may be necessary or desirable to carry out the purposes thereof.

IN WITNESS WHEREOF, I/We have hereunto set hand and seal this _____ day
of _____
Date of signing

WARNING: The date of signing must be the same as the date of execution of the application, if item (a) was checked above.

Date: 16th Jan 2001.
January 16, 2001

24 D. Sand - -
Signature of ASSIGNOR(S)

Date: _____

Date: _____

Date: _____

(if ASSIGNOR is a legal entity, complete the following information)

(type or print the name of the above person
authorized to sign on behalf of ASSIGNOR)

Title

NOTE No witnessing, notanzation or legalization is necessary. If the assignment is notarized or legalized, then it will only be prima facie evidence of execution. 35 USC 261. Use next page if notarization is desired.

☐ Notarization or Legalization Page Added.

(Assignment or Invention [16-3]—page 3 of 3)